Cummins-ORNL\ Emissions CRADA:
NO_x Control & Measurement Technology for Heavy-Duty Diesel Engines, Self-Diagnosing SmartCatalyst Systems

project ID: ACE032

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DOE Vehicle Technologies Office
Annual Merit Review & Peer Evaluation Meeting
June 9, 2016
Washington, DC

DOE Managers:
Gurpreet Singh, Ken Howden, Leo Breton

This presentation does not contain any proprietary, confidential, or otherwise restricted information

OAK RIDGE National Laboratory

Overview

Timeline

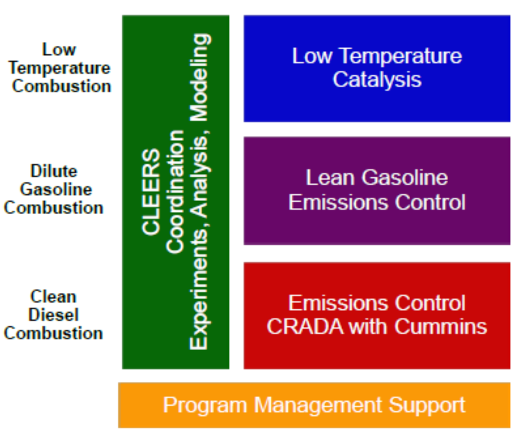
- Year 1 of 3-year program
- New 3-year CRADA extension
- Builds on FY13-FY15 R&D

Barriers

- *From DOE VT MYPP:*
  - 2.3.1.B: Cost-effective emission control
  - 2.3.1.C: Modeling for emission control
  - 2.3.1.E: Emissions-control durability

Budget

- 1:1 DOE:Cummins cost share
  - In-kind Cummins contribution
- FY16 DOE Funding: $300k
  - Task3: Cummins CRADA on Diesel Emissions Control
  - Part of ORNL project: “Enabling Fuel Efficient Engines by Controlling Emissions” (2015 VTO AOP Lab Call)



Partners

- **ORNL & Cummins Inc.**
- CLEERS
- Queen’s Univ. Belfast
- Univ. of Chem. & Tech. Prague

Objectives & Relevance

Objectives

- Enable & improve ***Predictive Catalyst-Performance Models***
  - Based on controlling physics & chemistry
  - Independent of specific application platform (e.g., truck, bus, boat, power)
- Characterize spatiotemporally distributed catalyst performance
  - Investigate ageing impacts (performance at different catalyst states)
  - Validate & improve models
  - Mine data & insights for OBD & control methodologies
- Develop methods for real-time catalyst-state assessment

Relevance

- Predictive models ***enhance engine-catalyst-system performance***
  - Design – improved design tools, more reliable analysis-led design
  - Development – faster & lower cost process, reduced component cost & size
  - In-Field Use – improved control, OBD, efficiency & durability
  - Enables improved emissions compliance & improved fuel economy
  - CLEERS Priority Survey ranks SCR aging mechanisms & models #4 (/64)
- Advances DOE goals for improving catalyst cost, modeling & durability

CRADA Approach

CRADA

Spatiotemporally Resolved Experiments

CRADA

Data

SS & Transient

Knowledge

Reaction network, Property correlations

CRADA

Structuring & validation of Predictive Models

Better models for improved design tools, OBD & control

Understanding performance-parameter correlations

Insights for better modeling, control & OBD

Ideas for Control & OBD

Enables improved efficiency, reliability & durability

Clean, Fuel-Efficient, Durable

Engines in the Marketplace

Cummins Development

Improved Durability & Performance

Improved Design Tools

Reduced Size & Cost

Better Control & OBD

Milestones

Completed all 2015 Milestones:

- ✓ **Q2:** Assess distributed performance of Field-Aged commercial SCR catalyst
- ✓ **Q3:** Present CRADA ageing insights at CLEERS Workshop

On track for meeting 2016 R&D objectives:

- Develop Step-Response method for determining catalyst-state parameter
- Assessment & development of predictive catalyst performance model
- Investigate common aspects of dynamic inhibition

Technical Progress: *Overview*

Enabling SmartCatalyst Systems

Tools & Models for better Design, OBD & Adaptive Control

Impacts of Field-Ageing & Adaption Methods

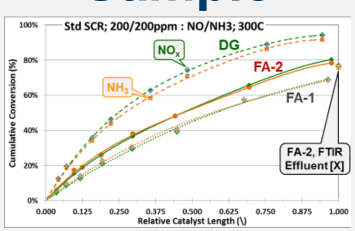
- Field-Aged sample compared to DeGreened
  - Lower SCR conversion and Total NH_3 Capacity
  - Same Dynamic NH_3 Capacity and adsorption energetics
  - Can use same adsorption model with scaling factor

FY 2015

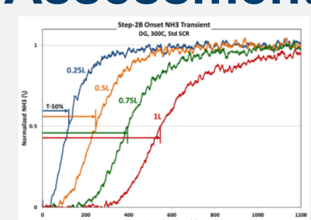
Are insights from FA-1 generally applicable?	Concept for catalyst-state assessment	Spaci data allows critical model assessment

FY 2016

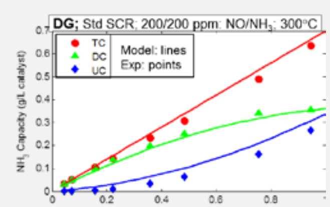
2nd Field-Aged Sample



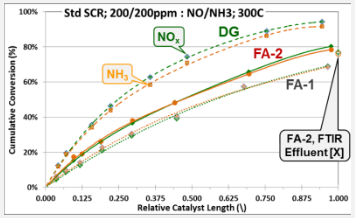
Method for State Assessment



Validate Cummins Predictive Model



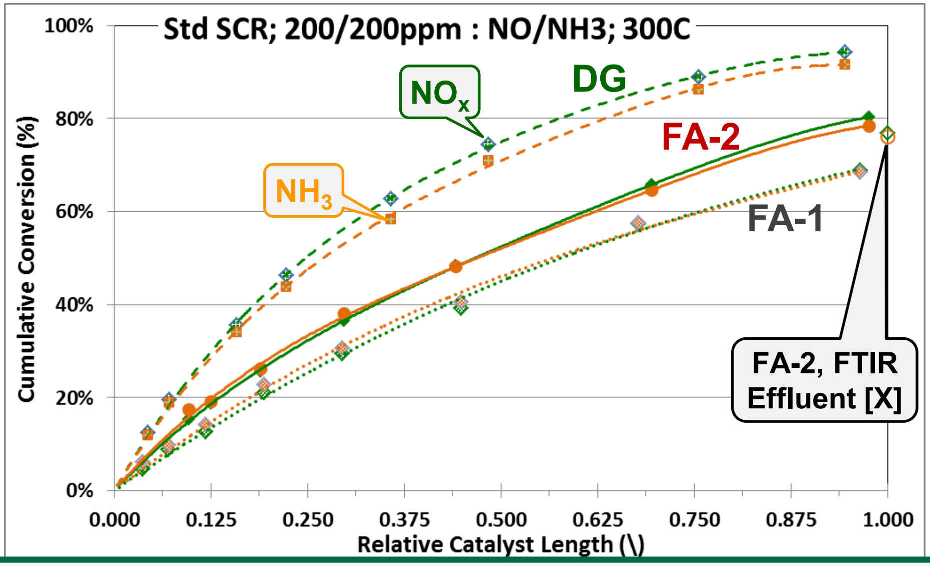
2^{nd} Field-Aged Sample

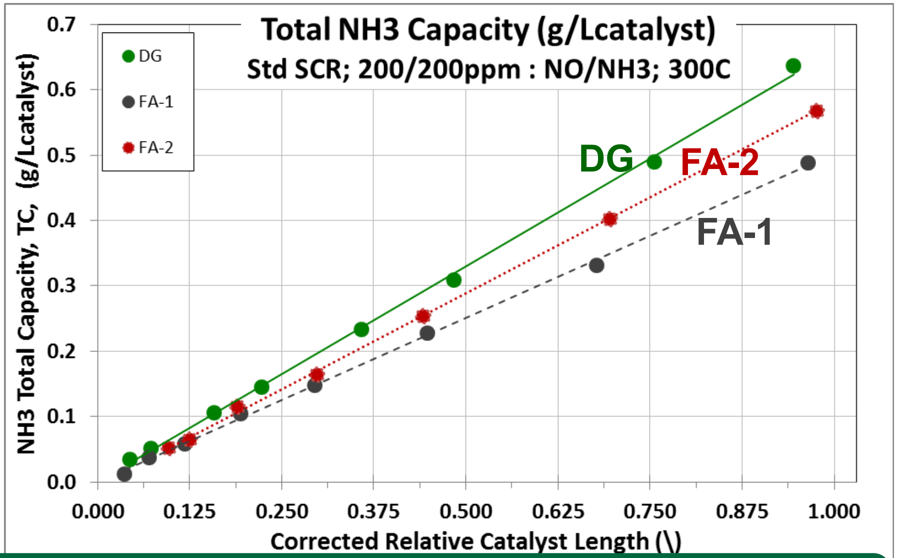


Tech.Prog.: Similar Impact from two Field-Aged Catalyst Samples

<u>Are FA-1 insights (2015 AMR) applicable to other Field-Aged (FA) samples?</u>

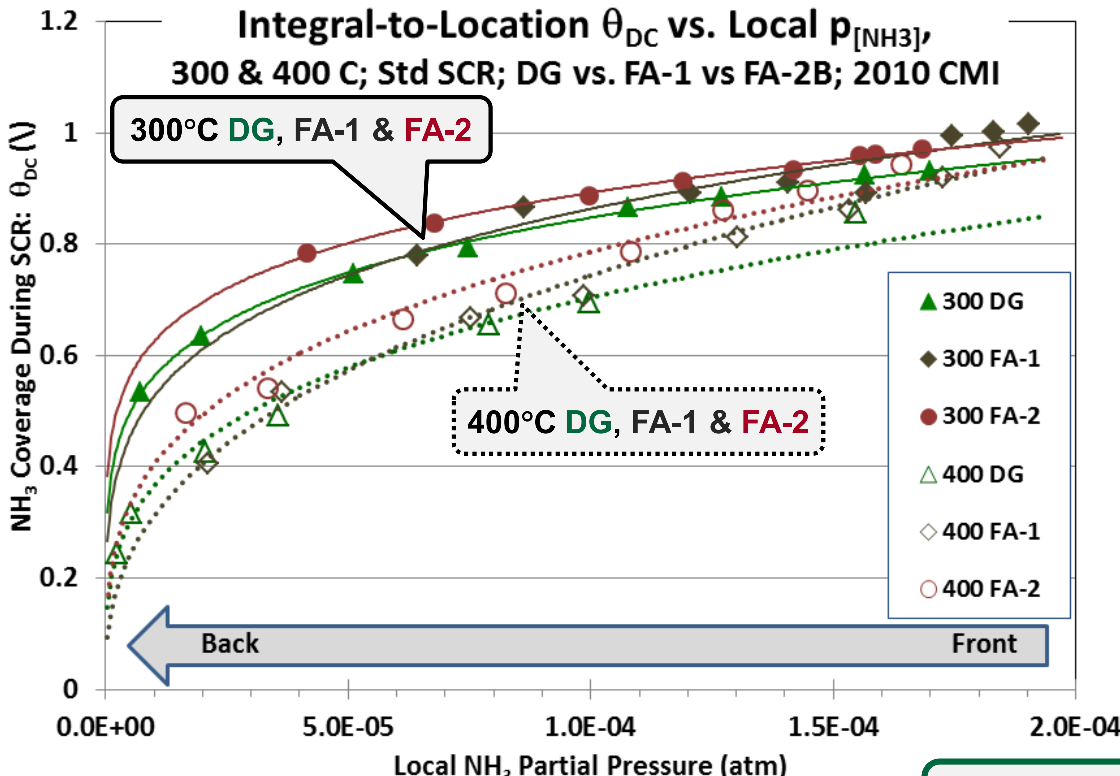
- Will a single predictive model work for different Field-Aged samples?
- Commercial 2010 Cummins, Cu/SAPO-34 SCR catalysts
  - Different field exposures; unknown exposure details; normal ageing profiles
  - Value – real-world on-road use; data to critically assess predictive model
- ***Two different field-aged samples show similar performance response***
  - Field ageing degrades conversion & Total NH_3 Capacity (**TC**)
  - Same capacity utilization correlations (cf. Backup Slides)
  - Does not change absorption energetics (cf. Operando Isotherms)





Similarities suggests FA-1 insights are applicable to other FA samples

Tech.Prog.: Field Ageing does not Practically Impact NH_3 Adsorption Energetics



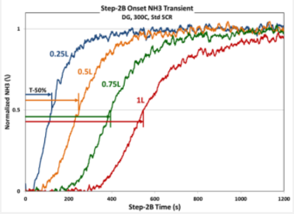
- *Operando isotherms*
  - Measured under SCR-reaction conditions: NO_x + NH_3
  - vs. 'neat' studies: without NO_x
- Shape of 2-site Langmuir
  - cf. neat CLEERS studies
- Selective adsorption-site ageing would change shape
  - ΔEnergetics → ΔShape

- Similar NH_3 adsorption energetics for three catalyst states: DG, FA-1 & FA-2
  - Same shape at a given temperature
  - Compliments CLEERS work (ACE032)
    - Neat isotherm studies; SSZ & SAPO
    - CRADA provides operando & ageing

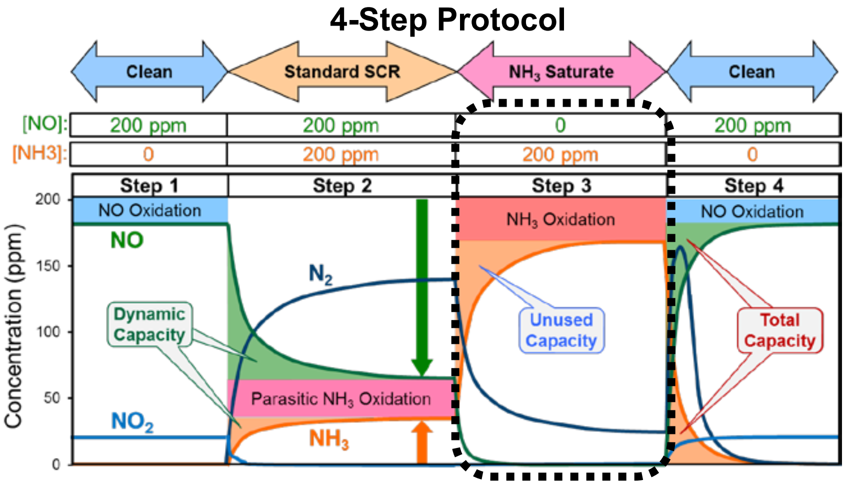
Simplifies modeling of aged samples
- Field ageing reduces number of sites
- But adsorption occurs in same way
- Use same model with scaling factor

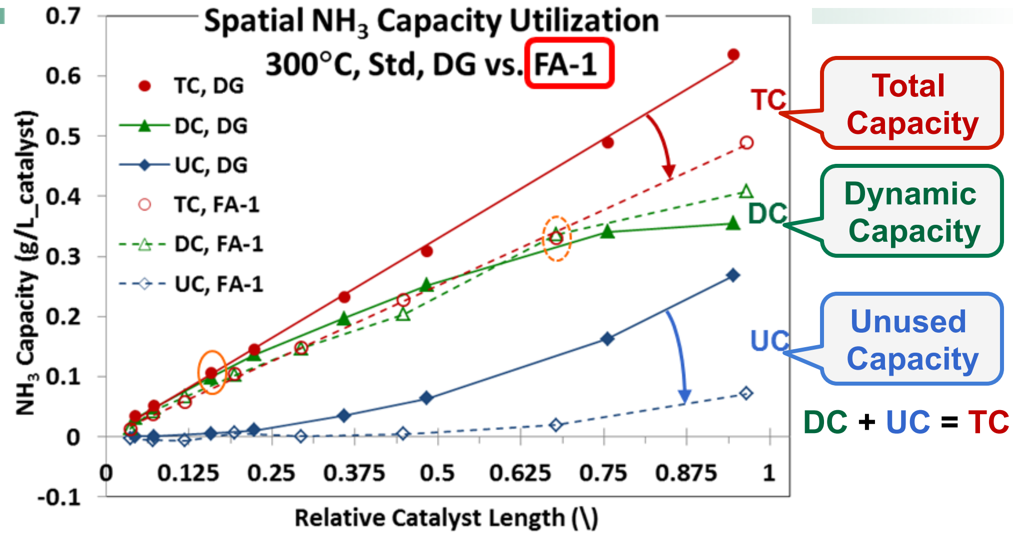
Need to determine catalyst state
- i.e., age-dependent **TC** & scaling factor

Method for State Assessment

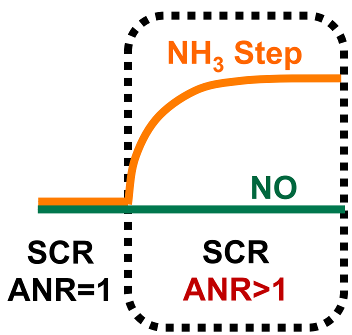


Tech.Prog.: Transient Response Measurement of Catalyst State





- **DC**, **UC** & **TC** capacity components determined from 4-Step Protocol
  - **UC** varies with catalyst state
    - **UC** & **TC** variations are related
    - Use to measure catayst state

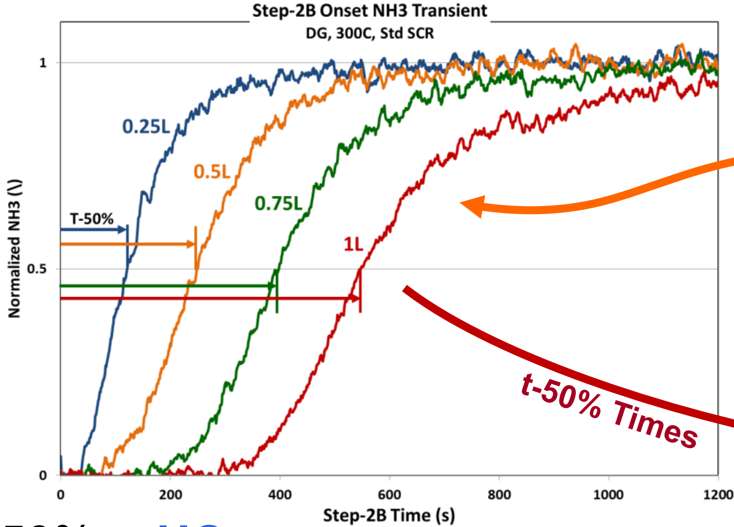


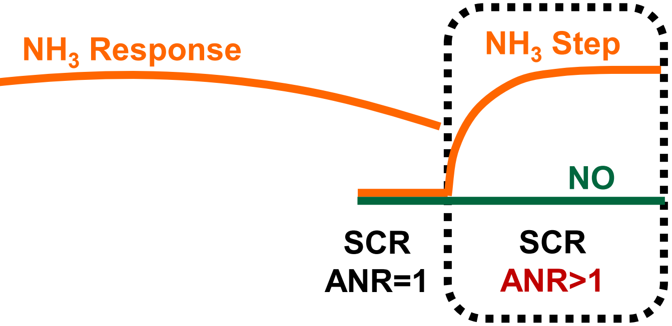
- Protocol not practical for on-road use
- NH_3 step response to probe **UC** variations
  - SCR continues with NH_3>NO
  - Could implement via dosing control

Use for active catalyst-state determination

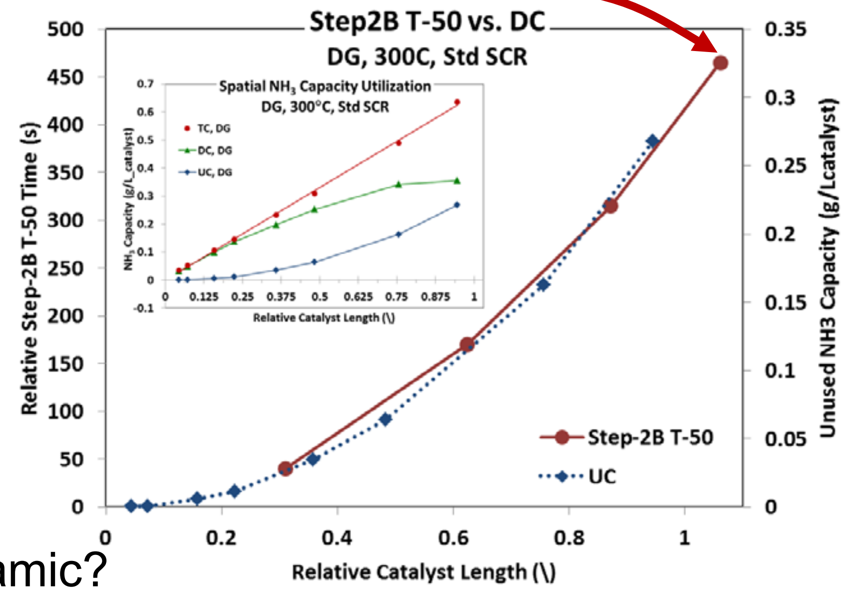
- Determine factors for feedback
  - e.g., **TC** scaling factor for predictive-model
- Enable OBD & adaptive control

Tech.Prog.: Stepped SCR Dosing to Determine TC Scaling Factor





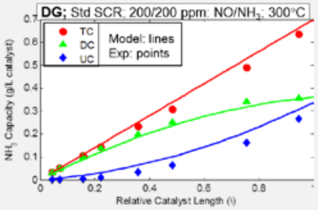
- t-50% ∝ **UC**
  - Varies with ageing; DG vs. FA
  - Possible to use other transient features
  - Alternate probes might be possible
- Many challenges remaining
  - What pulse & characteristic to use
  - Correlations with catalyst state & factors
  - Use probe pulse or natural drive-cycle dynamic?



Approach for practical catalyst-state assessment

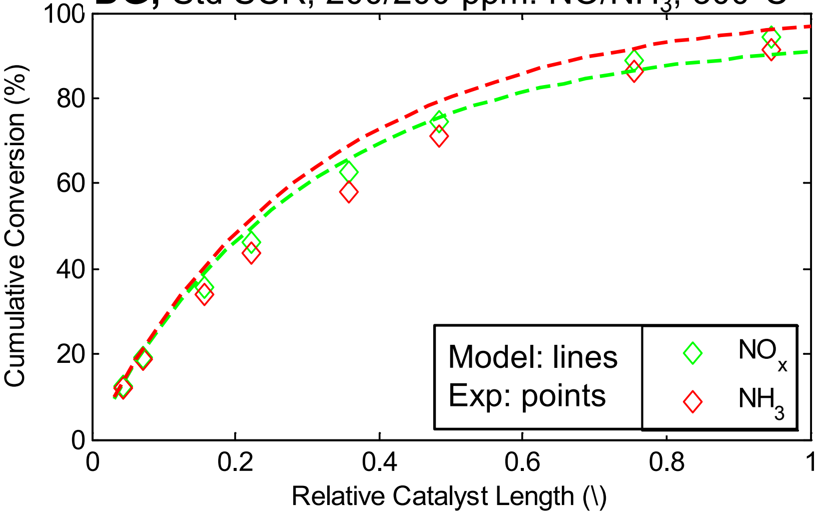
Pathway for thru-life OBD & feedback-enabled adaptive control

Validate Cummins Predictive Model

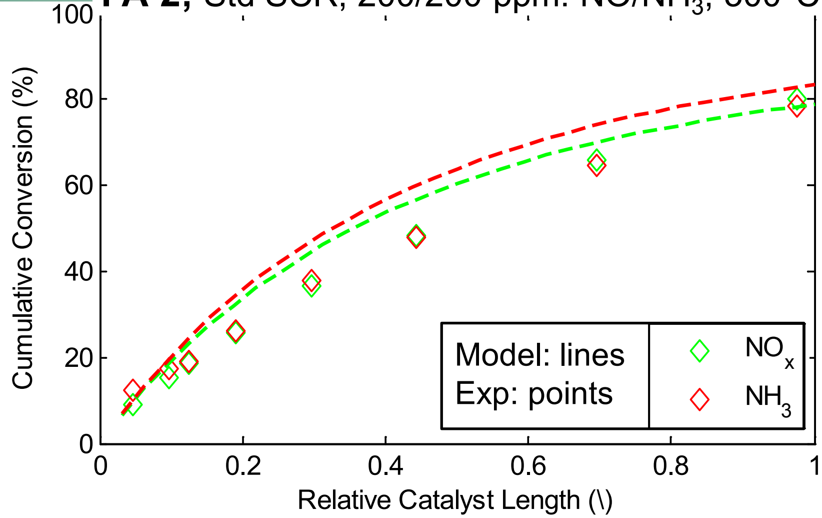


Tech.Prog.: Validating Cummins Kinetic-Model Structure; P1/2

DG; Std SCR; 200/200 ppm: NO/NH_3; 300°C



FA-2; Std SCR; 200/200 ppm: NO/NH_3; 300°C

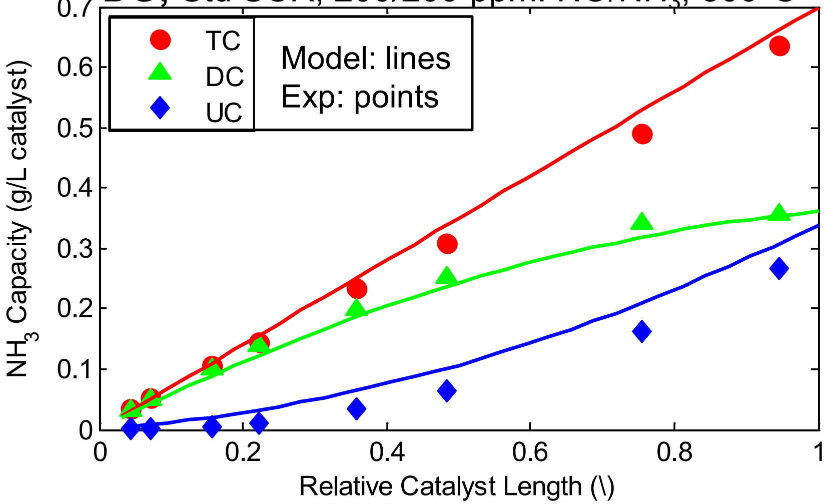


Goal: develop a predictive model to determine the catalyst's internal state

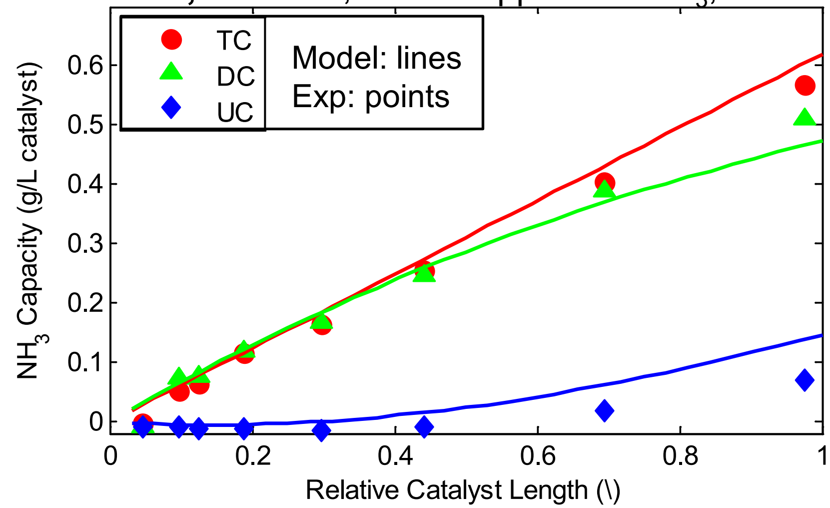
- Cummins' base predictive model is very complex
  - Many ways to structure & numerous model parameters to fit/determine
  - Developed based on integral DeGreened catalyst measurements
  - Run in AVL Boost
- Predictive model modifications for FA-2 sample
  - Reduced SCR reaction pre-exponential *(impacts conversion and DC distributions)*
  - Reduced integral TC *(impacts TC & UC distributions)*
- Model accurately predicts conversion distributions within the catalyst
  - Ability to predict intra-catalyst distributions a rigorous assessment test
    - Particularly for catalysts with internal storage functions like SCR and LNT

Tech.Prog.: Validating Cummins Kinetic-Model Structure; P2/2

DG; Std SCR; 200/200 ppm: NO/NH_3; 300°C



FA-2; Std SCR; 200/200 ppm: NO/NH_3; 300°C



- Model accurately predicts internal NH_3 capacity utilization
  - In different catalyst states: DG & FA-2
  - Relationships between **TC**, **DC** & **UC** components
  - Supports pathway for catalyst-state assessment; i.e., via **UC** measure

Predictive model rigorously validated vis-à-vis conversion & capacity distributions
– ***Confirms that model's internal workings are structured & fit properly***
– ***Enhances confidence in its use to design OBD & reduce design margins***

Next step is assessing transient performance

Responses to 2015 Review Comments

FY2015 AM5 Review
(5 Reviewers; max score: 4)

Category	Score
Approach	3.40
Tech Progress	3.40
Collaboration	3.60
Future Research	3.30
Weighted Average	**3.41**

Numerous Positive Comments:

- "excellent approach," "results always great"
- "solid technical accomplishments"
- "excellent collaborations"
- "solid proposed work to meet a very good plan"

Recommendations:

- ✓ Include transient behavior in the study
  - *Transients are included in the experimental protocols, and are used for capacity analysis*
  - *An additional transient–response protocol was developed and used this year; see results*
  - *Future work will focus on assessing the predictive model vis-à-vis measured transients*
- ✓ Identify strategies for catalyst-state assessment
  - *This is a major goal of the CRADA, and is one basis for the CRADA approach*
  - *A specific strategy was suggested last year, and others have been demonstrated in the CRADA*
  - *Early work in demonstrating such a strategy is presented this year*
- ✓ Take care to avoid duplication of effort (e.g., within ORNL)
  - *The CRADA works to avoid and does not duplicate efforts*
  - *The CRADA coordinates with CLEERS to compliment without duplicating efforts; e.g., spatially resolved ageing studies, field-aged samples, operando isotherm measurements*
- Better characterization (temp histogram) of field aged samples, and analysis of other axial & radial locations
  - *The field aged samples are from real-world exposure which does not log such detailed exposure data*
  - ✓ *The team works to maximize value and advance the CRADA & DOE goals within in budget constraints*
- Desire to know more regarding Cummins' contributions to the CRADA
  - ✓ *Both ORNL & Cummins contributing to planning & analysis; Cummins leads the modeling efforts*
- Suggest including automotive OEM's in the CRADA
  - ✓ *Such valuable broader input is received and incorporated via the AMR and ACEC Tech Team*
  - *The CRADA is a formal partnership between ORNL and Cummins*

Collaborations & Coordination with Other Institutions

- **Cummins**
  - CRADA Partner, Neal Currier (Co-PI)
- **CLEERS (ACE022, Pihl, Wednesday 4:15pm)**
  - Diagnostics, analysis & modeling coordination
- **UCT, Prague (Profs. Marek & Kočí)**
  - N_2O formation & control studies (**with CLEERS**)
  - David Mráček, et al. (2015). Appl. Catalysis B: Env. 182, 109-114.
  - Petr Kočí, et al., 24th NAM, 2015.
  - David Mráček et al., CAPoC10, 2015.
- **Politecnico di Milano (Profs. Tronconi & Nova)**
  - Mechanistic SCR studies (**with CLEERS**)
  - Maria Pia Ruggeri, et al. (2015). Appl. Catalysis B: Env.l 166, 181-192.
  - M.P. Ruggeri, et al. CAPoC10, 2015.
- **Queen's University, Belfast (Prof. Alex Goguet)**
  - Spatially resolved methods and analysis
  - Kevin Morgan, et al. (2016). ACS Catalysis 6, 1356-1381.
- **Publications, Presentations & Recognition**
  - 3 Archival Journal Publication, 4 Presentations
  - Invited journal publication & presentation
  - Spaci-approach highlighted on ACS Catalysis cover

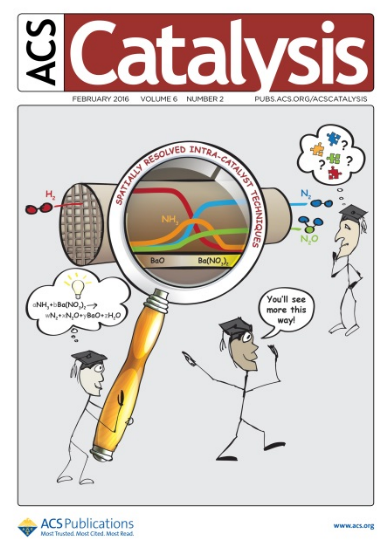
Cummins

CLEERS Cross Cut Lean Exhaust Emissions Reduction Simulations

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

POLITECNICO DI MILANO

Queen's University Belfast



Remaining Challenges & Barriers, and Proposed Future Work

Major Challenge: Improved catalyst Efficiency, Cost, Durability, OBD & Control
Solution: Develop Predictive Models & methods for Catalyst-State Assessment

- Spatially & temporally resolved intra-catalyst performance distributions
- Apply for model development & mine correlations for control strategies

Catalyst Sensing & Models

Challenges	Approach\Future Work (FY16-18):
Sensing catalyst state – Determine state-dependent parameters and variations throughout catalyst-system life – Improved OBD	Develop practical diagnostic methods – Advance insights from Pulse\Step-Response method – Investigate other transients and response features – Identify how to use natural drive-cycle features
Life-optimized catalyst performance – Enable through-life adaptive control based on sensor feedback	Develop robust physicochemical predictive models – Validate distributed transient performance – Adjust internal structure & complexity as required – Assess vis-à-vis other SCR catalysts & aged states
New insights to advance primary modeling & state-sensing objectives	Further detailed characterization & analysis – Incorporating & comparing to CLEERS data – Threshold aspects of dynamic inhibition – Radial & axially distributed ageing impacts

Work supports predictive model & state-sensor development for enabling improved catalyst efficiency, control, durability & cost

Summary

- **Relevance**
  - CRADA work enables improved catalyst knowledge, models, design & control
  - This reduces catalyst system costs & required engine-efficiency tradeoffs
  - This in turn enables DOE goals for improved fuel economy
- **Approach**
  - Develop & apply diagnostics to characterize catalyst nature
  - Analyze data to understand mechanistic details of catalyst functions & ageing impacts
  - Develop physicochemical predictive catalyst models based on improved catalyst knowledge
- **Technical Accomplishments**
  - Evaluate second Field Aged sample, FA-2
    - Compare distributed performance with DG & FA-1 samples; identify parameter correlations
  - Demonstrate practical method for catalyst-state assessment
  - Validated internal structure and fit of Cummins predictive catalyst model
    - Via distributed steady-state performance; transient assessment is next
- **Collaborations**
  - Numerous university collaborations resulting in presentations, publications and advances
  - Coordination & collaboration with other DOE projects to maximize benefit
- **Future Work**
  - Apply data & insights to improve catalyst predictive models & catalyst-state assessment
  - Analysis to understand transient catalyst performance & common parameter thresholds
  - Evaluation of alternate ageing conditions, sample locations and catalyst types

Technical Back-Up Slides

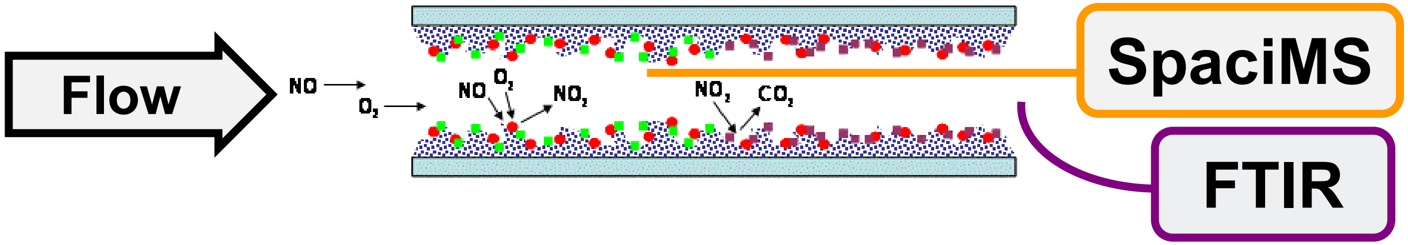
Experimental: Catalyst, Conditions, Methods & Approach

	Commercial
Catalyst	2010 CMI, Cu/SAPO-34
Mini-Core size	21 cells; ca. 2.45-cm long x 0.78 wide
Channel density	300 cpsi (FA2 is 400)
Space Velocity	40,000 hr^{-1}
NH_3, NO_x	200ppm, 200ppm
Base O_2 & H_2O	10% & 5%
Temperatures	200, 300 & 400°C
Standard SCR	✓ focus of these slides
Fast SCR	✓
Diagnostic	SpaciMS & FTIR, CMI 4-Step Protocol

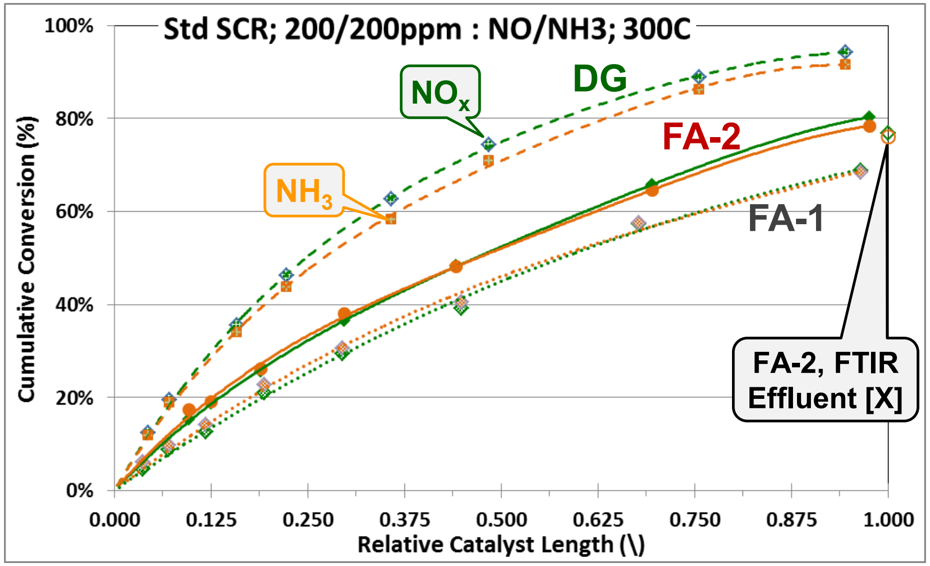
State	Conditions
DeGreened (**DeG**)	700°C, 4hrs, 10%O_2 + 5%H_2O; • From front of sample B11-22

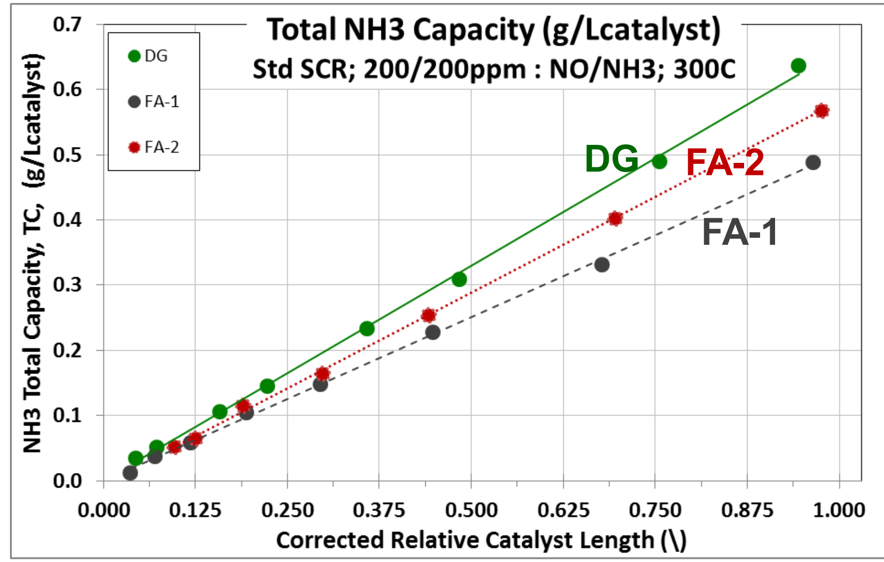
Field Ageing (**FA1**)	Prepared by CMI;
	• CMI date: 7-1-2014
	• Normal ageing profile
	• From front of larger sample;
	• Pretreatment at ORNL:
	  • 500°C to remove HC & S
	  • Cycling at 200, 300 & 400C to steady state

Field Ageing (**FA2**)	Prepared by CMI; • Provided: 9-9-2015 • Normal ageing profileFA-2A: as received • FA-2B: High T Treatment • Baseline mix; 500°C, 2hr



Tech.Prog.: Assessing Differences in Two Field-Aged Catalysts

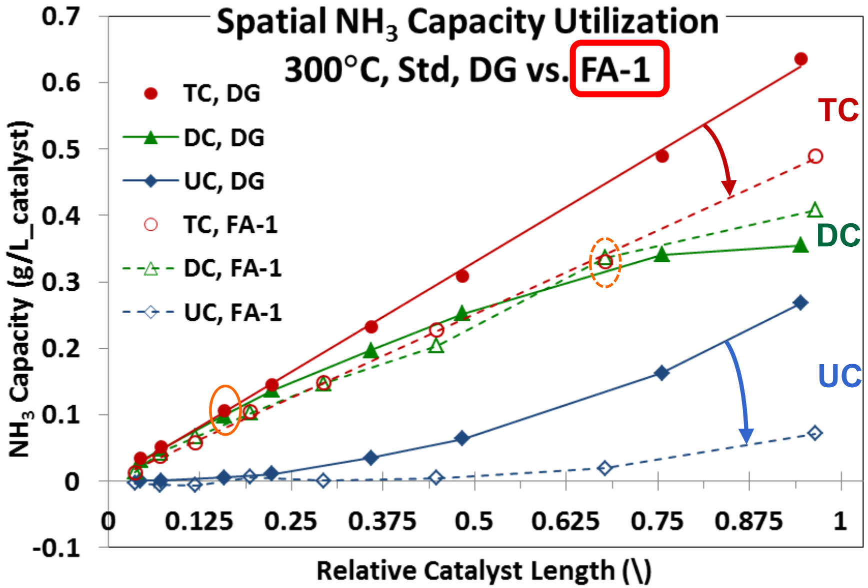


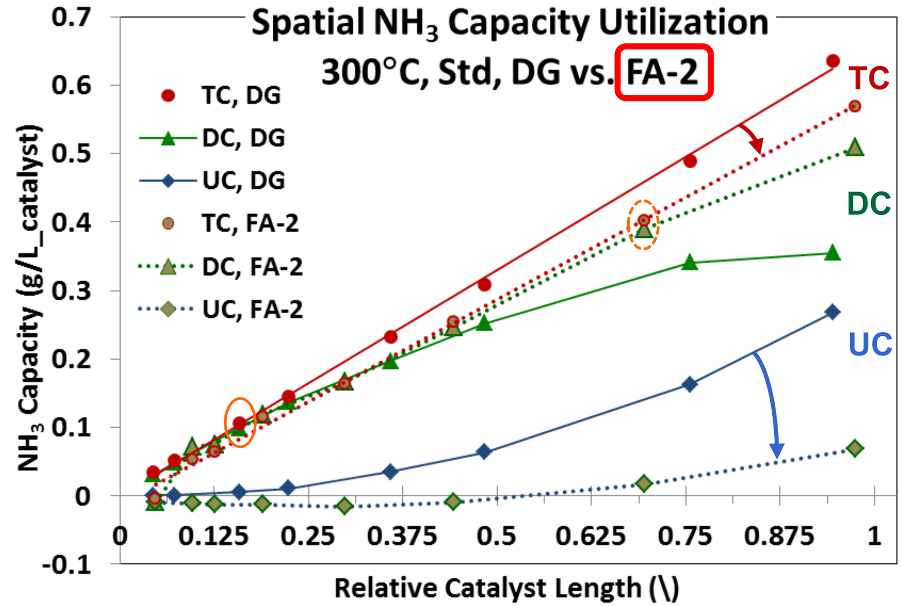


Are FA-1 insights (2015 AMR) applicable to other field-aged (FA) samples?

- Will a single predictive model work for different Field-Aged samples?
- Commercial 2010 CMI, Cu/SAPO-34 SCR catalysts
  - Different field exposures; unknown exposure details; normal ageing profiles
  - Value – real-world on-road use; data to critically assess predictive model
- Field ageing degrades conversion and Total NH_3 Capacity (TC)
  - Generally similar although different absolute impacts
  - Better FA-2 conversion consistent with greater TC
  - Similarities suggests FA-1 insights may be applicable to other FA samples
- Using data to assess Cummins' predictive models

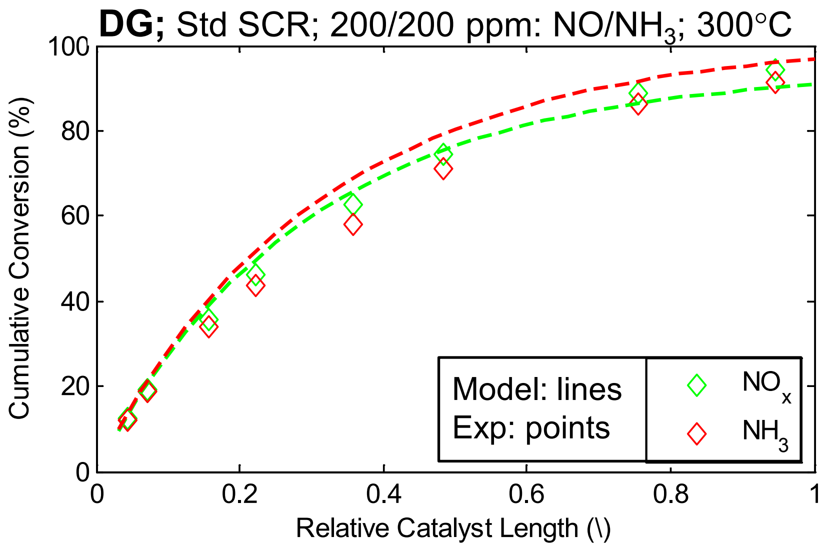
Tech.Prog.: NH_3 Capacity Utilization Similar for Field Aged Samples

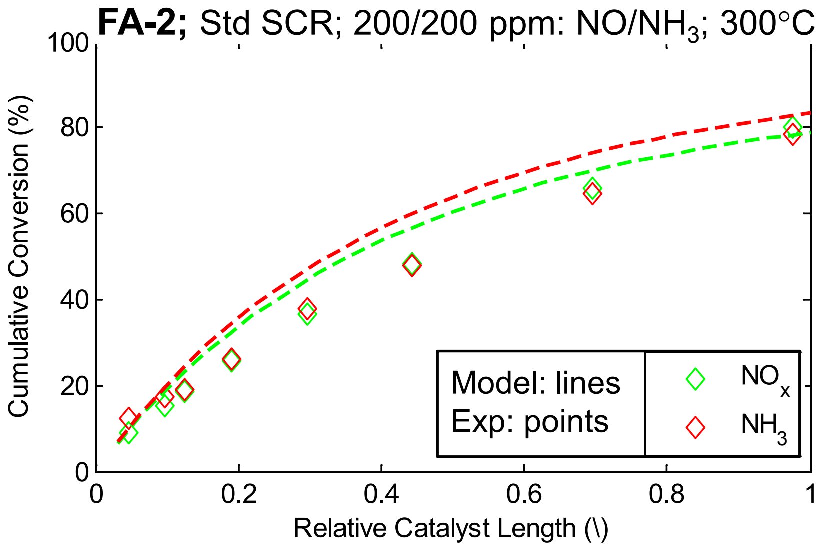


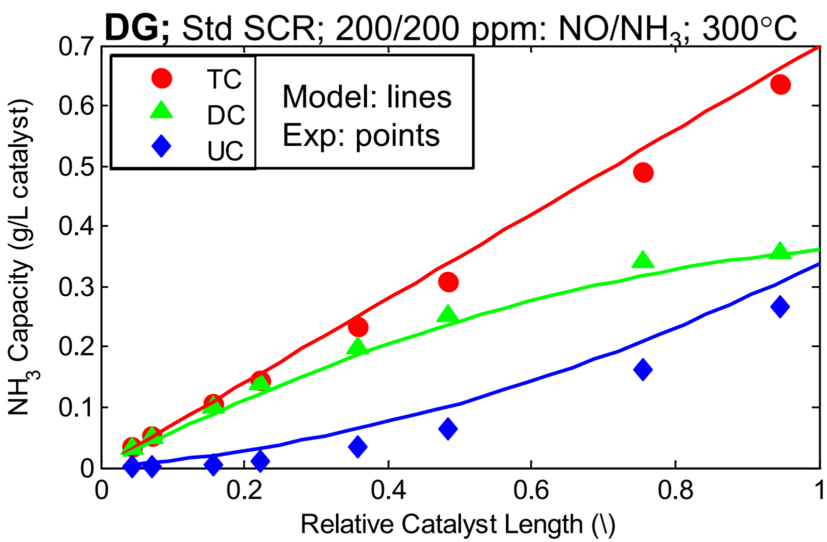


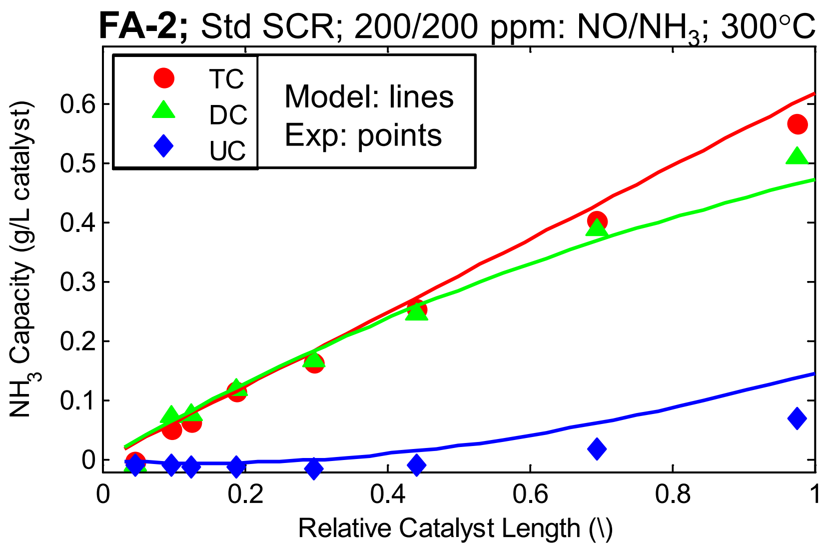
- Three NH_3 Capacity Components: Total (**TC**), Dynamic (**DC**), Unused (**UC**)
  - DC is fraction used during SCR; **DC** + **UC** = **TC**
- Field ageing has systematic impact on NH_3 capacity utilization & distributions
  - Reduces Total Capacity, TC
  - Lower SCR rate extends SCR deeper into the catalyst
    - Reduces DC-TC separation; separation occurs deeper into the catalyst
    - Reduces Unused Capacity, UC
- Ageing state and capacity utilization are correlated
  - Use capacity to determine catalyst state and state-dependent parameters

Tech.Prog.: Spaci Used to Validate Kinetic Model Structure

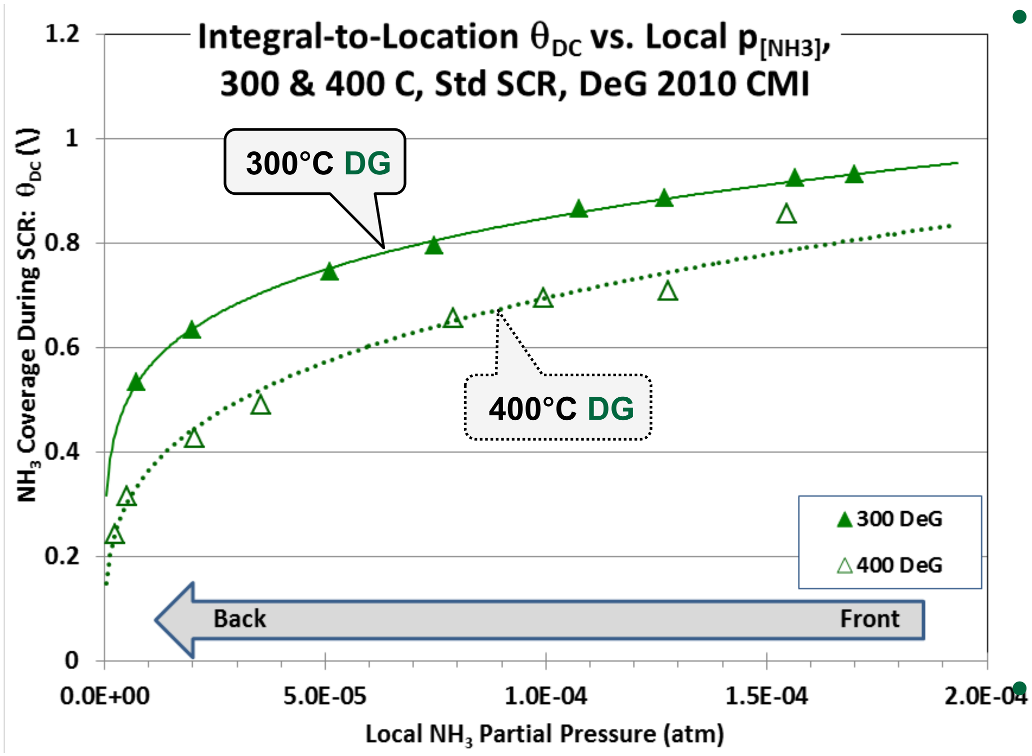


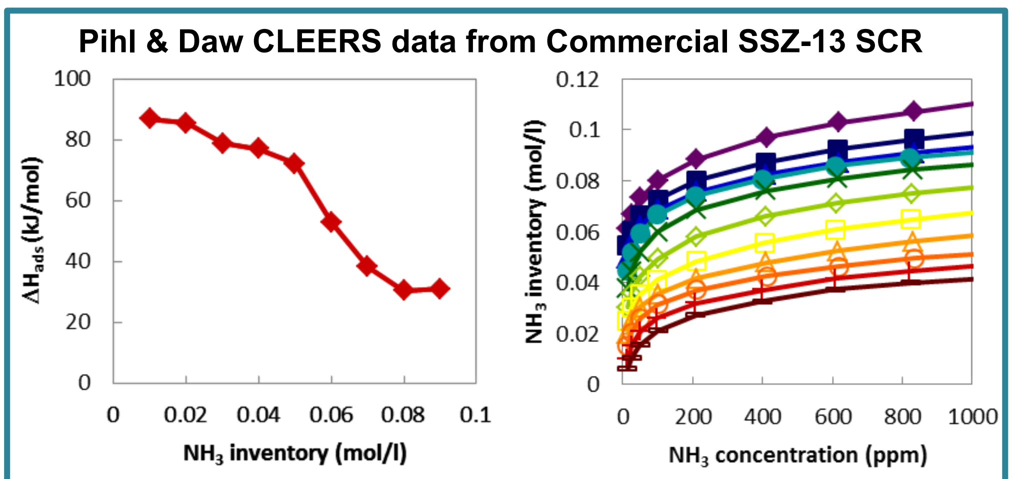






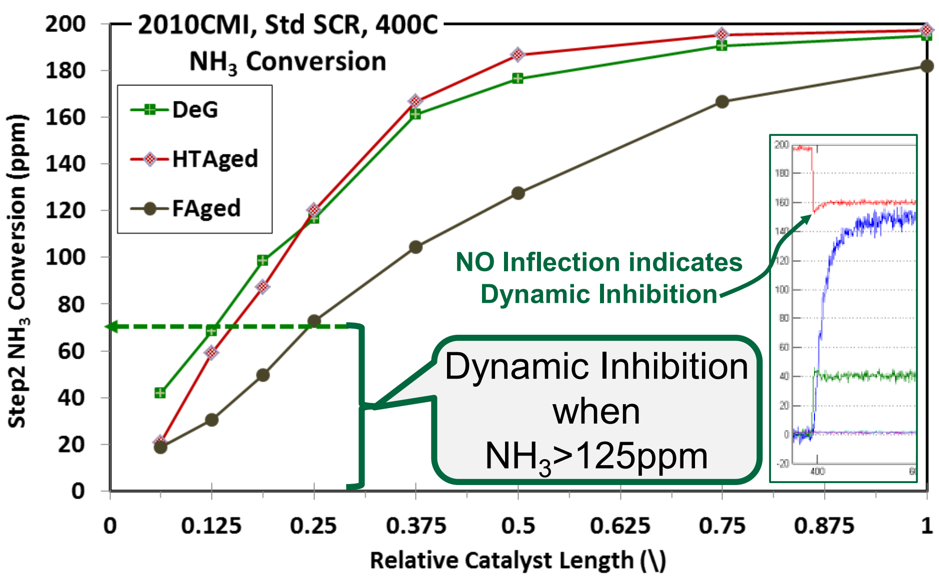
Adsorption Isotherm has Characteristics of 2-Site Langmuir





- NH_3 Isotherm from SpaciMS data
  - ***Under SCR reaction conditions***
    - Isotherm has extra loss term: reaction
  - Normalized coverage shown
    - DC / (DC + UC)
  - Adsorption is faster than even Fast SCR
    - Implied by DC-TC separation at a common $[NH_3]$ for Standard & Fast SCR (previously shown)
  - Can interpret isotherm classically
- Shape is like 2-site Langmuir
  - See Pihl & Daw CLEERS data
    - From commercial SSZ-13 SCR
    - Model fit with uniform partitioning between the ca. 80 & 30kJ/mol sites
  - Distinct knee at low NH_3 partial pressure
- Isotherm flattens at higher temperature
  - Typical nature for Langmuir isotherm

Field Ageing Does Not Change Dynamic NH_3 Inhibition



Tronconi, Cat.Today 105, p529; describes dynamic inhibition

- 'modified redox (MR) SCR rate law'
- Depends on T, C_{NO}, θ_{NH3} & C_{O2}

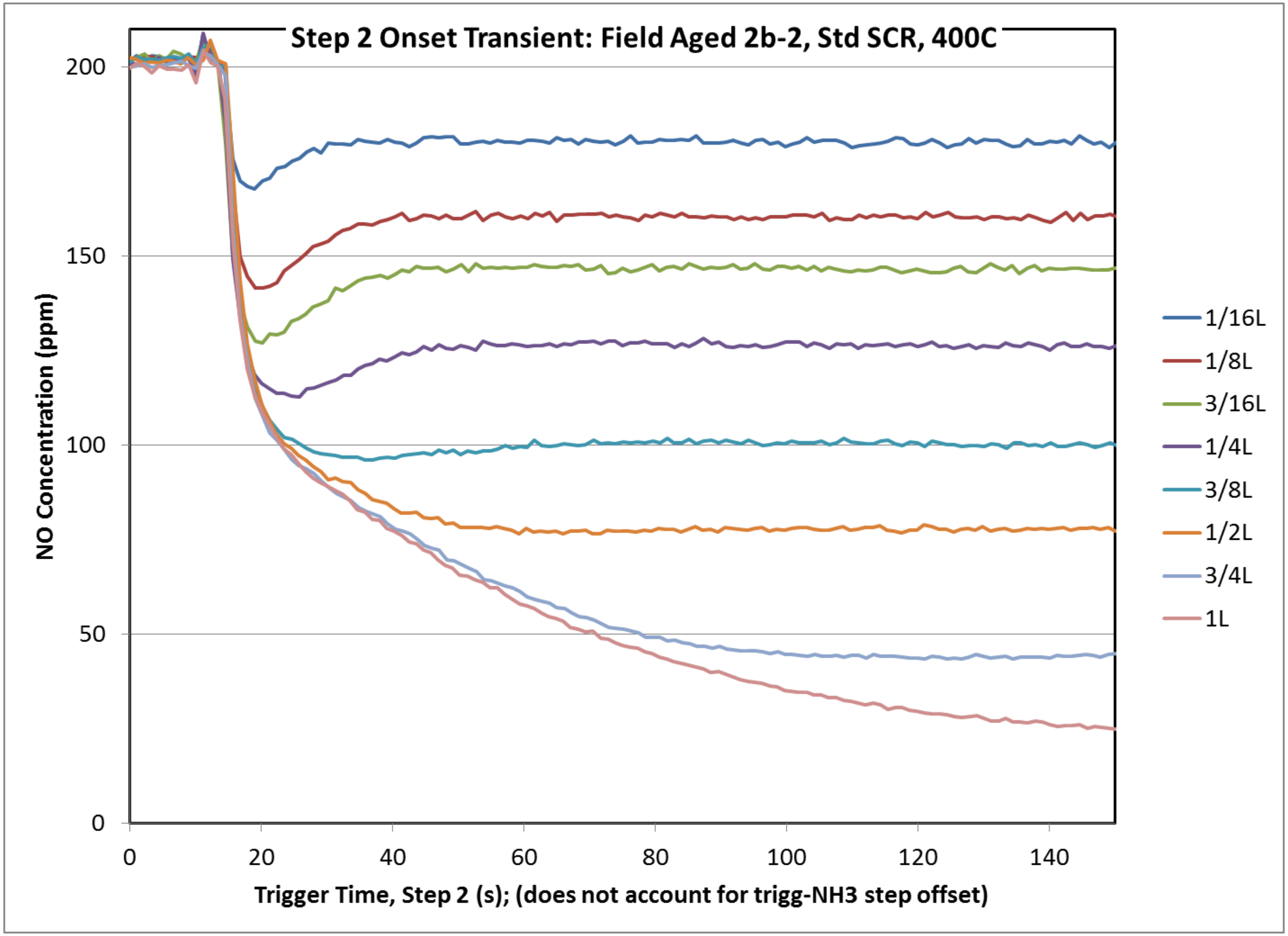
$$r_{NO} = \frac{k'_{NO} O' \exp\left(-\frac{E_{NO}}{RT}\right) C_{NO}\theta_{NH_3}}{1 + K'_{NH_3}\frac{\theta_{NH_3}}{1-\theta_{NH_3}}}\left(\frac{p_{O_2}}{0.02}\right)^{\beta} \qquad (12)$$

- r_{NO}: rate of DeNOx reaction
- E_{NO}: Activation energy for DeNOx reaction
- C_{NO}: gas phase concentration of NO
- θ_{NH3}: surface coverage of NH_3
- k_{NO}: pre-exponential factor for DeNOx reaction rate constant
- K_{NH3}: NH_3 rate parameter
- p_{O2}: O_2 partial pressure
- **S1: redox site for O_2 & NO adsorption/activation**
- **S2: acidic site for NH_3 adsorption**

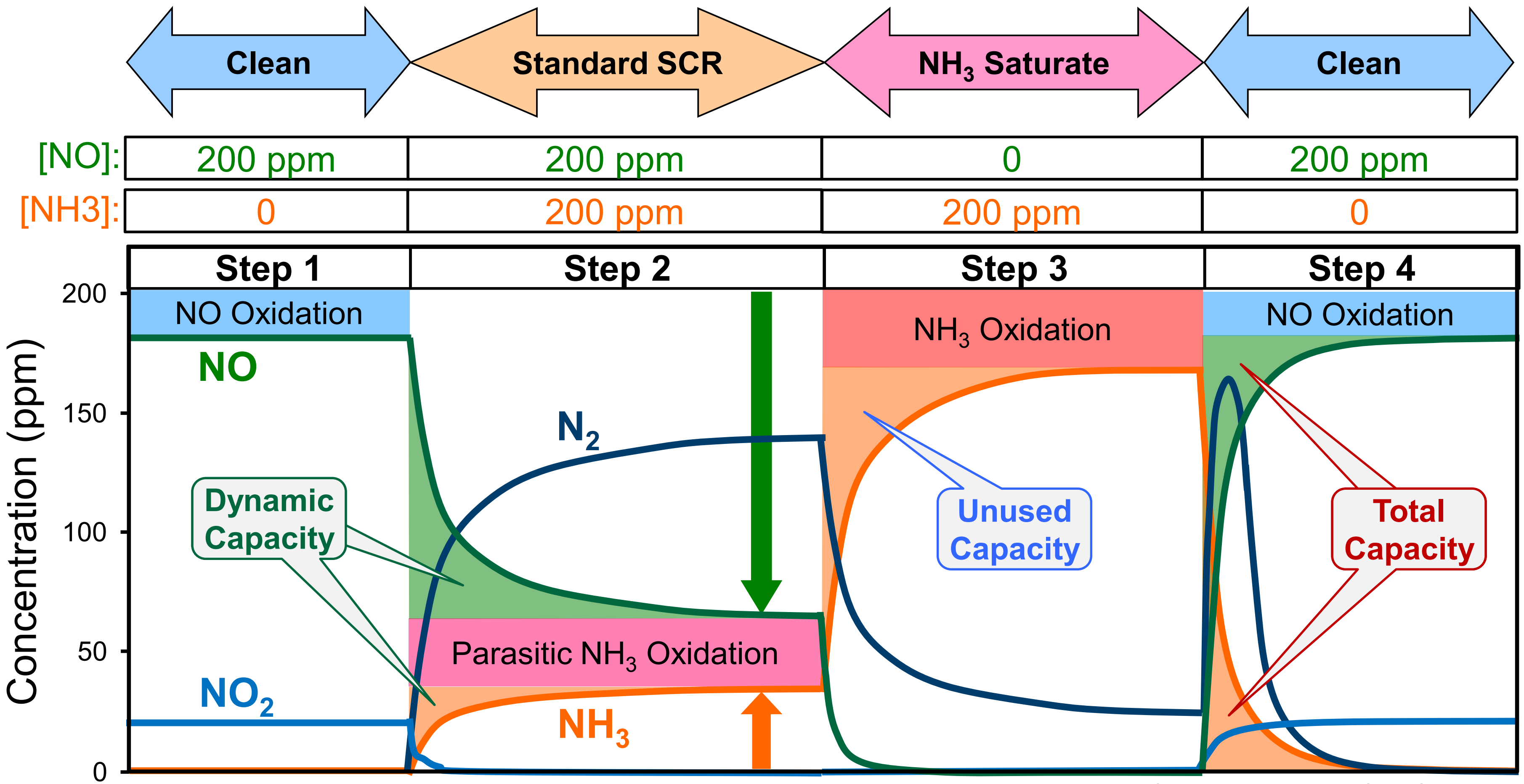
- Dynamic inhibition at SCR start
  - Observed in catalyst front for all samples
  - ***Observed above consistent [NH_3] limit***
    - ≳ 165ppm [NH_3] at 300°C
    - ≳ 125ppm [NH_3] at 400°C
      - 400°C more sensitive
      - Due to faster reaction or less accessible DC?
      - More sensitive to spillover from Higher-E S2 sites, which are more dominant at high-T
  - Impacts NO & NH_3 adsorption parameters

- ***Suggests inhibiting NH_3 & NO interactions not impacted by FA***
  - *Abundance of S2 vs S1 sites*
    - *i.e., NH_3 spillover from S2 to S1 is equivalent in DG & FA; even with lower FA TC*
    - *Consistent with lower NH_3 vs. NO capacity*
    - *Consistent with separate S1 & S2 sites*
    - *Can lose many S2 sites before change in NO-adsorption inhibition occurs*
    - *FA selectively impacts S2 sites over S1?*

Dynamic NH_3 Inhibition Exist Deep Into FA-2 Catalyst Sample



Cummins 4-Step Protocol Resolves Reaction Parameters



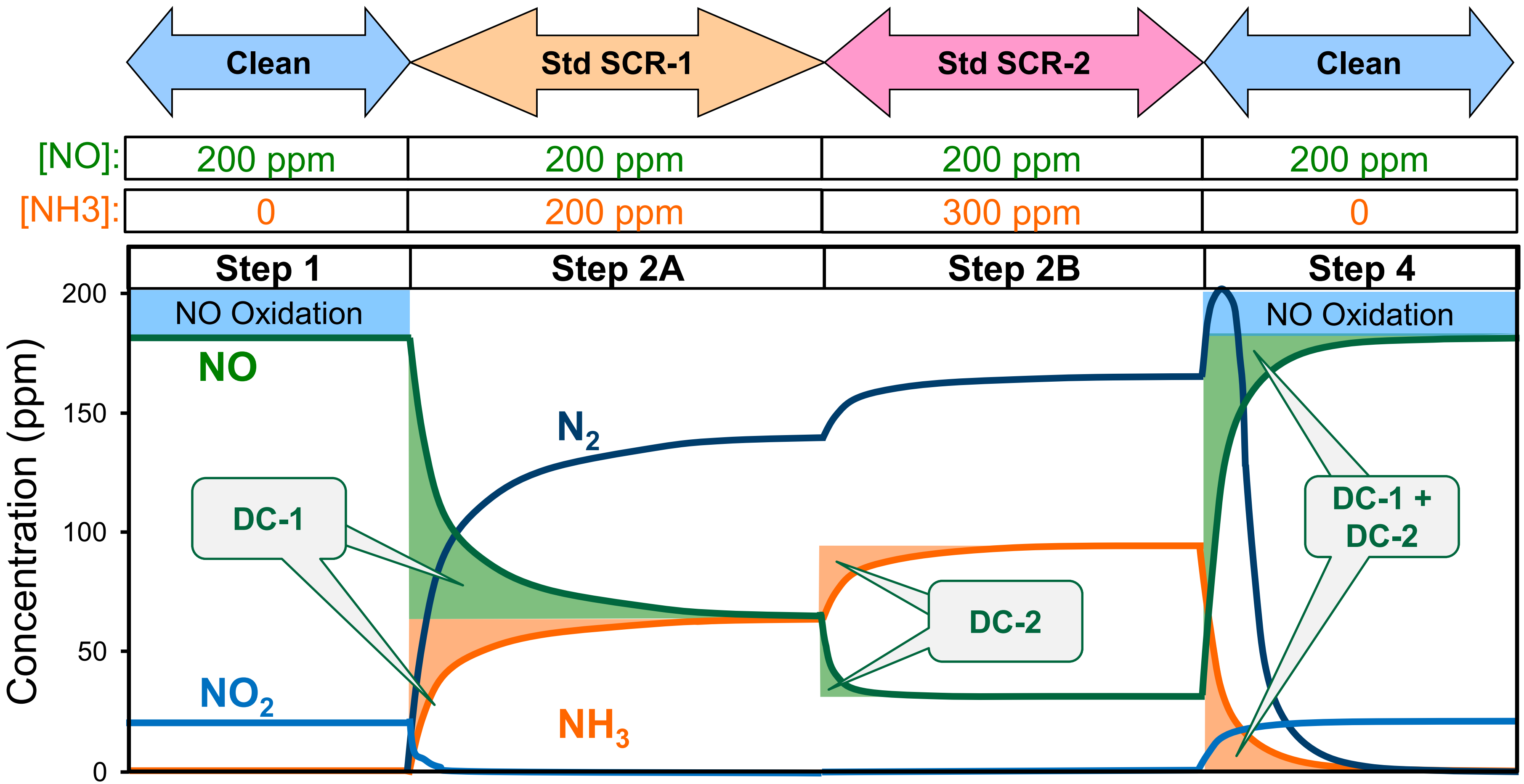
K. Kamasamudram, et al., Catalysis Today 151(2010) 212-222.

- Step1: NO oxidation
- Step2: SS NO_x & NH_3 conversions, Parasitic NH_3 oxidation, Dynamic NH_3 capacity
- Step3: NO_x-free NH_3 oxidation, Unused NH_3 capacity
- Step4: NO oxidation, Total NH_3 capacity

Total = Dynamic + Unused

for the Department of Energy

Pulsed/Step-Response Protocol



- Step1: NO oxidation
- Step2A: DC-1 from SCR with ANR=1
- Step2B: DC-2 from SCR with ANR>1 Step4: Separate determination of DC-1 + DC-2